Geochemical fingerprints and controls in the sediments of an urban river: River Manzanares, Madrid (Spain)

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Abstract

The geochemical fingerprint of sediment retrieved from the banks of the River Manzanares as it passes through the City of Madrid is presented here. The river collects the effluent water from several Waste Water Treatment (WWT) plants in and around the city, such that, at low flows, up to 60% of the flow has been treated. A total of 18 bank-sediment cores were collected along the course of the river, down to its confluence with the Jarama river, to the south–east of Madrid. Trace and major elements in each sample were extracted following a double protocol: (a) "Total" digestion with HNO_3, $HClO_4$ and HF; (b) "Weak" digestion with sodium acetate buffered to pH=5 with acetic acid, under constant stirring. The digests thus obtained were subsequently analysed by ICP-AES, except for Hg which was extracted with aqua regia and sodium chloride-hydroxylamine sulfate, and analysed by Cold Vapour-AAS. X-ray diffraction was additionally employed to determine the mineralogical composition of the samples. Uni- and multivariate analyses of the chemical data reveal the influence of Madrid on the geochemistry of Manzanares' sediments, clearly manifested by a marked increase in the concentration of typically "urban" elements Ag, Cr, Cu, Pb and Zn, downstream of the intersection of the river with the city's perimeter. The highest concentrations of these elements appear to be associated with illegal or accidental dumping of waste materials, and with the uncontrolled incorporation of untreated urban runoff to the river. The natural matrix of the sediment is characterised by fairly constant concentrations of Ce, La and Y, whereas changes in the lithology intersected by the river cause corresponding variations in Ca–Mg and Al–Na contents. In the final stretch of the river, the presence of carbonate materials seems to exert a strong geochemical control on the amount of Zn and, to a lesser extent, Cu immobilised in the sediments. This fact suggests that a variable but significant proportion of both elements may be susceptible to reincorporation in the aqueous phase under realistic environmental conditions.

1. Introduction

The need to gain a better understanding of the behaviour of urban environments and the consequences of living within or close to a city's boundaries is clearly justified by the fact that cities have become the habitat where 2.7 billion people, or 47% of the total world population are currently housed. Furthermore, the (U.N. Population Division (UNPD) (2001)) estimates that nearly all the population growth in the next 30 years will be concentrated in the urban areas of the world. If this projection is accurate, 5.1 billion people will live in cities in 2030 and the percentage of urban population will accordingly increase to 60% of the world's total. If the statistical analysis is restricted to the more developed regions, it is estimated that the percentage of urban population in 2030 will reach 83.5%, up from 76% in 2000 (U.N. Population Division (UNPD), 1996, 2001; World Bank, 2000).

With the growing interest in the rules that govern the fate of pollutants in urban environments, the sediments of urban rivers pose a particularly challenging scientific problem. As in natural environments, urban river sediments have a high potential for storage of trace elements. Unlike natural rivers, however, a large proportion of the trace element load contained in urban sediments is not associated with the original geologic parent material, but with the steady supply of trace elements, both dissolved and in particulate form, carried by treated and untreated urban waters. Changes in the aqueous environment to which urban sediments are exposed could result in the release of these trace elements that have accumulated over long periods of time. The linkage between the concentration of toxic elements in the sediment and ecosystem health explain the growing interest and the—consequent—rapid increase in scientific publications dealing with metals in fluvial sediments (Sutherland, 2000).

A further complication in the study of urban rivers arises from the fact that their hydrodynamic behaviour is sometimes profoundly altered as they run through a city. Urban rivers are often canalised, the flow of water is regulated, some sections of the river can be isolated and the water in them removed for cleaning operations, during which sediments are dredged and/or exposed to the atmosphere, etc. All these factors combine to make predictions about deposition and geochemical behaviour of urban sediments quite uncertain. Within this context, River Manzanares constitutes an excellent example of an urban river with a strong anthropic control on its hydrodynamic behaviour and the geochemistry of its sediments. After passing through the city of Madrid, a large proportion of the water carried by River Manzanares is of urban origin and has entered the stream as discharge from five Waste Water Treatment (WWT) Plants that collect and treat the street runoff and domestic waste water (combined sewer system) of Madrid and a few nearby smaller towns. The river receives approximately 5.3×10^8 m^3 of treated water from Madrid every year. The percentage of treated urban water in River Manzanares varies from approximately 20% in wet years to 60% in years with low precipitation.

1.1. Description of River Manzanares

The river rises at an altitude of 2160 m in the granite mountains of Sierra de Guadarrama, north of Madrid. For 90 km, River Manzanares follows a southeast direction (Fig. 1), until it meets with the Jarama river shortly after exiting the urban perimeter of Madrid (pop. 3 million). Between the granitic Sierra and the city of Madrid, the Manzanares crosses Quaternary detrital materials, primarily gravel, sand and silt. Two major dams in the northern-most section of the river (Embalse de Santillana and El Pardo) control the flow of water arriving at the first of several weirs operated by Madrid's municipality. Four small streams between the first dam and Madrid and three downstream of the city—some of which flow only intermittently—contribute minor amounts of water to the River Manzanares. As it flows through the central part of the city, the river is canalised. Before and after this culverted section, small sections of the river banks are stabilised with large, angular boulders or rip-rap. South of Madrid, the River Manzanares flows through a landscape dominated by gypsiferous marls, clays and gypsum, intercalated with lenses of limestone.

2. Methods and materials

Eighteen sampling stations were positioned along the course of the River Manzanares (Fig. 1). The first four were located between the river's source and the

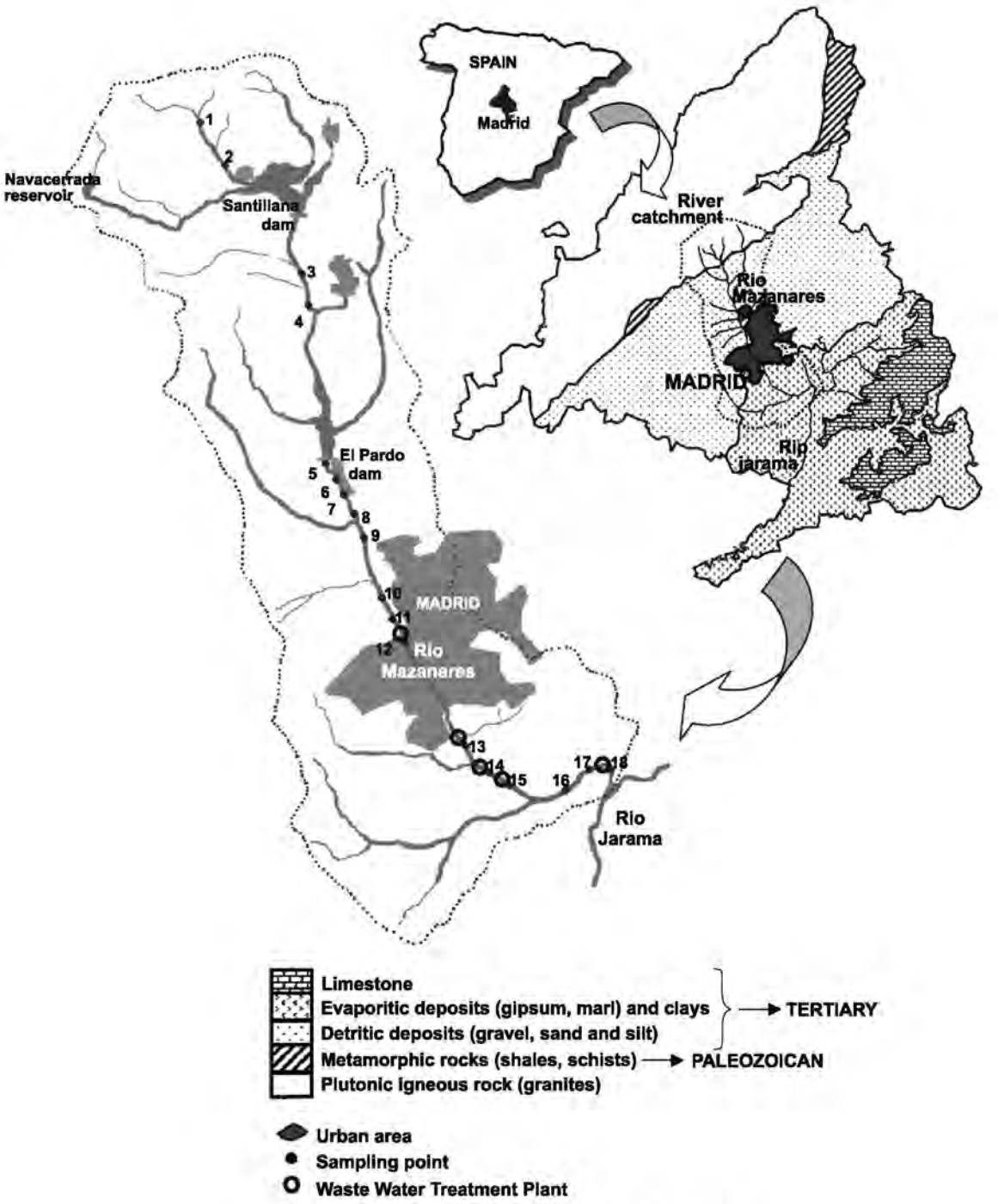

Fig. 1. River Manzanares basin and location of sampling points.

Table 1
Analytical results (μg g $^{-1}$) of the "total" digestion (HNO_3+$HClO_4$+HF); in italic, values below the method's detection limit (see text)

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Mean
Ag	*1.3*	*1.1*	*0.25*	*0.06*	3	2	2	2	2	4	5	*0.51*	16	7	5	4	9	9	4.1
Al	93600	93500	87700	88000	81100	88800	61900	77600	81900	68600	72800	70300	67000	73000	65900	59700	65000	56900	75183
As	*17*	*18*	*4.2*	*4.2*	25	*9.7*	57	34	23	36	*9.9*	*10.1*	39	27	31	25	*10.2*	29	23
Ba	284	266	266	250	352	498	29	586	377	44	445	429	140	418	343	154	193	388	303
Be	6	6	7	7	6	8	6	6	5	5	6	4	5	5	4	4	5	4	5.5
Ca	8300	5200	6000	3500	6300	5400	10100	6200	8300	14200	4400	8800	27600	16600	82300	80200	31600	71100	22561
Ce	139	183	126	104	148	158	136	193	182	115	185	47	135	142	68	131	203	138	141
Co	5	4	5	5	6	6	9	5	5	6	5	5	8	5	9	6	6	8	6
Cr	25	30	23	21	59	25	33	19	18	27	29	26	126	30	46	36	52	61	38
Cu	11	12	42	49	27	29	144	19	31	55	44	49	347	64	93	62	94	100	71
Fe	19100	20400	26000	20100	22100	27600	90800	19800	22000	29000	19500	22400	38400	23000	30000	21900	23400	26000	27861
Hg	*0.025*	*0.025*	*0.025*	0.196	0.072	0.217	0.076	0.085	0.671	1.776	0.234	0.805	0.528	0.708	0.792	1.241	0.931	0.234	0.48
K	27200	25400	21900	21900	32800	27800	21100	28600	26900	26500	27700	27300	24700	27700	43800	24900	26900	22200	26961
La	70	89	60	49	69	79	66	97	94	61	101	23	71	76	40	71	107	76	72
Mg	5800	4500	5300	4400	4500	5800	7000	5000	6800	5900	5600	4100	14900	7000	11400	9800	7600	14600	7222
Mn	359	305	399	396	503	578	1276	724	649	408	430	308	381	409	469	370	371	332	481
Na	18200	17900	15000	13100	19200	15500	11700	16100	13500	12900	15500	15500	13700	16000	6400	10900	14300	10400	14211
Ni	*9.4*	11	*7.4*	*5.3*	47	12	33	12	*4.9*	18	19	12	36	14	23	19	26	29	19
P	639	737	1090	876	927	737	1297	812	850	1001	1040	913	1568	1432	992	1049	1618	1487	1059
Pb	93	74	171	44	56	42	207	74	44	87	93	95	371	126	107	104	179	150	118
Ti	1800	2000	1500	1500	2700	3100	2200	3300	3400	2700	3000	1800	2900	3100	3600	2700	3100	2900	2628
V	28	28	28	29	28	33	29	26	25	28	23	24	44	29	57	32	26	39	31
Y	37	36	28	24	30	32	26	31	29	23	29	20	26	27	17	26	31	25	28
Zn	74	70	113	97	79	102	182	84	81	178	124	152	591	198	313	258	439	393	196

Table 2
Analytical results (μg g^{-1}) of the "weak" digestion (NaOHAc, HOAc); in italic, values below the method's detection limit (see text)

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Mean
Ba	19	15	23	23	25	22	35	34	22	15	15	14	18	16	13	16	26	13	20
Be	0.62	0.57	0.79	0.93	0.81	0.71	0.74	0.60	0.65	0.37	0.57	0.39	0.46	0.42	0.43	0.46	0.42	0.47	0.58
Ce	2.4	1.3	2.1	3.7	3.5	2.2	3.0	2.3	2.8	1.8	1.9	*0.86*	4.0	5.7	1.4	1.4	3.8	1.8	2.5
Cr	0.64	*0.45*	0.63	1.5	1.5	1.5	4.1	*0.49*	*0.46*	1.3	1.5	0.83	2.3	1.4	4.0	3.6	3.6	1.2	1.7
Cu	*0.12*	*0.047*	*1.0*	2.3	3.3	*0.78*	4.7	*0.63*	4.8	18	4.7	2.6	8.6	4.5	7.6	33	14	15	7
K	920	1088	435	460	1290	460	465	173	340	250	698	343	345	395	610	488	753	425	552
Mg	158	*0.61*	65	32	277	*1.5*	102	48	190	575	130	210	662	698	345	710	840	255	280
Mn	54	10	75	79	275	151	153	270	173	393	131	33	91	159	65	39	64	114	129
Ni	*0.021*	*0.013*	*0.10*	*0.97*	*9.6*	*0.32*	18	*0.87*	0.96	27	*1.42*	*1.65*	3.9	4.8	5.3	9.6	6.9	24	6.4
P	*18*	*15*	*18*	*11*	44	*21*	*24*	37	109	*23*	103	145	66	68	174	111	106	136	68
Pb	15	9.5	40	8.6	6.1	2.9	7.2	13	19	36	17	13	24	39	30	112	27	17	24
V	*0.44*	*0.35*	*0.49*	0.63	0.59	0.54	1.1	0.55	0.65	*0.32*	*0.46*	0.70	1.1	1.4	0.79	1.5	0.74	1.4	0.76
Y	2.2	1.5	1.2	2.1	1.8	1.1	1.9	1.3	1.5	1.4	1.1	0.50	2.0	2.4	0.83	0.98	2.1	1.1	1.5
Zn	4.4	4.5	4.7	6.0	15	4.8	14	8.2	43	39	35	55	79	148	166	182	127	64	56

first major dam, El Pardo dam; seven between this dam and the first WWT plant; one directly before the culverted stretch of the river in the city of Madrid; one immediately downstream of the second, third and fourth WWT plants, respectively; two more between the fourth and fifth WWT plants; and a last one downstream of the fifth WWT plant and close to the confluence of the Manzanares with the Jarama river (Fig. 1).

Sediment cores were retrieved from the upper 20 cm of the river bank, a few centimeters below the water level (and thus representing material that is periodically exposed to the atmosphere in the Summer months and during low-flow episodes) with an Eijkelkamp® riverside auger or a piston sampler. The samples were then transferred to air-tight plastic bags and transported in a portable refrigerator to the laboratory. All samples were oven-dried at 50 °C for 48 h, manually disaggregated and sieved to recover the <50 μm fraction (considered to represent the silt-clay fraction of the sediment). Three subsamples were subsequently separated for "total" and "weak" digestions, and for Hg analysis.

From the first subsample 1 g was transferred to a Teflon reactor where a mixture of 5 ml HNO_3 (70% v/v), 5 ml $HClO_4$ (70% v/v), and 10 ml HF (48% v/v) was added. The solution was then heated to dryness in an open hot-plate, and the residue redissolved with 5 ml HCl (36% v/v) and 20 ml MilliQ water. The resulting solution was filtered and transferred to a 100 ml volumetric flask. This analytical protocol is assumed to dissolve the silicate matrix of the sample and thus yield a "total" digest.

A second 1 g subsample was subjected to a "weak" digestion with 1 M sodium acetate (NaOHAc), buffered to pH 5 with acetic acid (HOAc, 99.5% v/v), under constant stirring for 5 h. The solution thus obtained was filtered and transferred to a 25 ml volumetric flask. This protocol coincides with the second step in Tessier's sequential extraction procedure (Tessier et al., 1979) and the "weak" digest is presumed to represent the fraction of the sediment that could become mobile and bioavailable under realistic environmental conditions.

Preparation of a third subsample for Hg analysis followed US Environmental Protection Agency's Method 7471A (US Environmental Protection Agency, 1994): 0.2 g of sediment was mixed with 5 ml deionised water and 5 ml aqua regia, and the solution

was then heated for 2 min in a water bath at 95 °C. After cooling, 50 ml deionised water and 15 ml 5% $KMnO_4$ were added to the solution. The solution was then heated again for 30 min, allowed to cool, 6 ml of sodium chloride-hydroxylamine sulphate were added to the solution, and the volume was made up to 100 ml with deionised water.

All samples were analysed for 17 trace elements and 6 major elements (Table 1) by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) while Hg concentrations were determined by Cold Vapour-Atomic Absorption Spectrometry (CV-AAS) at the Laboratory of Inorganic Analysis of the Spanish Geological Survey (IGME). Reagent blanks and standard reference materials, i.e. NIST SRM 2704, river sediment (Epstein et al., 1989), were used for quality control. The analytical results for Ag, As, Al, Ca, Co, Fe, La, Na and Ti in the sodium acetate–acetic acid extraction were below the method's detection limit in more than 50% of all observations or did not pass the repeatability standards in the quality control guidelines, and were consequently omitted from the corresponding database (Table 2).

Analytical results below the method's detection limit (in italics in Table 1 and Table 2), when present in less than 50% of all the observations for a given variable, were substituted by the arithmetic mean of the three actual readings of the ICP-AES for that sample. For Mercury, however, the laboratory did not supply the original readings and observations below the detection limit were replaced with half the value of the detection limit.

Additionally, the mineral matrix of the samples was characterised by X-ray Diffraction (XRD), including preparation of oriented aggregates, ethylene glycol swelling tests for smectite and thermal treatment for kaolinite.

3. Description and interpretation of results

Tables 1 and 2 show the results of the elemental analyses after the "total" and "weak" digestions, respectively. Results of the X-ray diffraction analyses are presented in Table 3. Univariate analysis of the data for the "total" digestion shows, in the first place, the anomalous nature of samples 7 and 13. Sample 7, marked by high concentrations of total As and Fe (57 and 90800 $\mu g\ g^{-1}$, respectively), was collected from a station where the section of the river becomes deep and narrow, creating a pool in which sediments accumulate preferentially. XRD analysis of the sample reveals the presence of pyrite in concentrations close to 10%, a fact that would explain the elevated levels of total As and Fe. It is unclear whether the accumulation of pyrite is the result of illegal or accidental disposal of mining/industrial wastes, or whether it is associated with the transport and deposition, in this low-velocity reach, of sulphide materials found in mineral deposits and abandoned mining sites located upstream from station 7. Sample 13 was taken just downstream of the second WWT plant, which collects and treats urban runoff and domestic waste waters from Madrid's city centre. The highest concentrations of total Ag (16 $\mu g\ g^{-1}$), Cr (126 $\mu g\ g^{-1}$), Cu (347 $\mu g\ g^{-1}$), Pb (371 $\mu g\ g^{-1}$) and Zn (591 $\mu g\ g^{-1}$) were found at this location. This elemental association is characteristic of urban particulate materials (soil and street dust), but also of discharges from WWT plants (Birch et al., 2001), sewage sludge produced in WWT plants, and of the

Table 3
Results of the X-ray diffraction analyses

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
%Quartz	30	28	27	31	22	28	24	36	28	36	34	28	30	37	25	22	31	33
%Plagioclase	31	23	16	19	28	16	12	13	14	13	11	10	17	16	6	11	19	10
%K Feldspar	8	16	10	8	20	21	11	13	13	13	15	12	7	11	9	9	13	6
%Calcite	–	–	–	–	–	–	–	3	3	3	1	15	5	3	20	17	6	18
%Dolomite	2	2	3	–	2	1	1	3	1	3	3	2	3	1	3	4	2	5
%Phyllosilicate	29	31	44	42	28	34	42	32	41	32	36	33	38	32	37	37	29	28
%Smectite	–	–	–	–	12	12	17	14	30	14	22	10	14	10	8	13	9	7
%Mica	18	17	18	19	16	18	25	18	11	18	14	23	24	22	22	24	20	21
%Vermiculite	11	14	26	14	–	–	–	–	–	–	–	–	–	–	7	–	–	–
%Kaolinite	–	–	–	9	–	4	–	–	–	–	–	–	–	–	–	–	–	–

Table 4a
Comparative analysis of trace element concentration (μg g^{-1}) in urban river sediments

		Ag	As	Cr	Cu	Fe (%)	Mn	Ni	Pb	Zn
River Henares, Spain[a]				(97–180)	(7–270)	(0.8–3.16)	(150–445)		(11–128)	(17–1280)
River Seine, France[b]					*84*	*2.91*			*162*	*429*
	Upstream				*15.1*			*40.9*	*120*	*343*
River Sowe, UK[c]	Urban area				*47.9*			*164*	*411*	*786*
	Downstream				*18.6*			*103*	*234*	*496*
Semarang, Indonesia[d]					(12.3–448)				(5.2–2666)	(53.7–1257)
Danube River, Austria[e]					*43.5*				*53.9*	*187*
Tiber River, Italy[f]				(18.2–54.2)	(13.3–45.5)			(3.6–33.5)	(12.4–43.1)	(53.4–417.6)
River Po, Italy[g]			(5.8–10.9)	(118–233)	(45.2–179.9)	(4.5–5.2)	(355–1159)	(99–237)	(39.3–71.8)	(127–519)
River Sherbourne[h]					(7.1–270)			(30–843)	(45.7–957)	(114–1586)
		4.1	*23*	*38*	*71*	*2.9*	*481*	*19*	*118*	*196*
River Manzanares		(0.1–16)	(4.2–57)	(18–126)	(11–347)	(1.9–9.1)	(305–1276)	(5–47)	(42–371)	(70–591)

In brackets: minimum–maximum values; in italic: arithmetic mean.
[a] Alarcón (1990).
[b] Estèbe et al. (1997).
[c] Foster et al. (1996).
[d] Widianarko et al. (2000).
[e] Gundacker (2000).
[f] Minissi et al. (1998).
[g] Vignati et al. (2003).
[h] Foster and Charlesworth (1996).

compost prepared with it (De Miguel et al., 1998). It is therefore possible that the elevated levels of "urban" elements in these sediments are associated with discharges from the WWT plant or, more likely, with the direct supply of untreated urban runoff to the river (Walker et al., 1999). This last hypothesis is supported by the proximity of the sampling station to an abandoned, illegal dump site whose effluents are suspected to reach the river course without entering the sewage system.

Although direct comparisons of the results of different investigations are complicated by the dispar-

Table 4b
Comparative analysis with toxicological reference values for river sediments (units in μg g^{-1})

Element	US DOE[a]			Canadian EQG[b]		US EPA[c]	Ontario MOE[d]	Manzanares
	Threshold effect concentration	Probable effect concentration	High no effect concentration	Interim sediment quality guideline	Probable effect level	Toxicity reference value	Lowest effect level	Arithmetic mean
Ag						4.5	0.5	4.1
Al		58030	73160			14000		75183
As	12.1	57	92.9	5.9	17	6	6	22.8
Ba						20		303
Co							50	6
Cr	56	159	312	37.3	90	26	26	38
Cu	28	77.7	54.8	35.7	197	16	16	71
Hg				0.170	0.486		0.2	0.480
Ni	39.6	38.5	37.9			16	16	19
Pb	34.2	396	68.7	35	91.3	31	31	118
Zn	159	1532	541	123	315	110	120	196

[a] Jones et al. (1997).
[b] Environment Canada (2002).
[c] US Environmental Protection Agency (1999).
[d] Ontario Ministry of Environment and Energy (1998).

ity in sampling protocols, digestion procedures of the samples, and the intensity of industrial discharges into the river, the concentrations of trace elements in the sediments of the Manzanares seem to fall in the same range as those found in other urban rivers, i.e. the Seine, Sherbourne, Henares, Semarang, Danube, Tiber, and Po (Table 4a). However, when compared with effects-based toxicological levels the situation is quite different (Table 4b). The mean concentrations determined for the River Manzanares are higher than Ontario's Lowest Effect Levels and than the US EPA's Toxicity Reference Values for all trace elements, with the exceptions of Co and Ag. Similarly, all of the Canadian Sediment Quality Guidelines are exceeded and the average concentrations of As and Pb in the Manzanares are even higher than the respective Probable Effect Levels (PELs), with the mean Hg concentration being almost identical to the corresponding PEL. Lastly, the Threshold Effect Concentrations defined by the U.S. Department of Energy (U.S. DOE) for As, Cu, Pb and Zn are surpassed by the average concentration of these same elements in the sediments of the Manzanares; for Cu and Pb even the high No Effect Concentrations are exceeded. A comparison with only those samples retrieved from stations within or downstream of Madrid is even more unfavourable, all of which seems to indicate that the levels of trace elements found in the sediments of river Manzanares might result in adverse effects on the aquatic ecosystems associated with this river, especially after it receives urban waters originating in Madrid.

In order to describe better and interpret the results of the multiple chemical variables analysed by ICP-AES and AAS, a number of multivariate statistical techniques were employed, i.e. Hierarchical Cluster Analysis, Direct Partition (K-means Cluster Analysis), and Factor Analysis. Cluster Analysis of observations for the "total" digest reveals three main groups of samples (Fig. 2). All the sediment cores collected upstream of the urban perimeter of Madrid (samples 1–9), with the exception of anomalous sample 7, are grouped together (Cluster 1 in Fig. 2). Samples taken inside or downstream of Madrid, down to the confluence of the Manzanares with the Jarama River, on the other hand, are divided in two groups (clusters 2 and 3 in Fig. 2). The reason for this separation is that samples 15, 16 and 18, which make up Cluster 3, represent the highest contents in calcium carbonate, with Ca concentrations at least twice as high as those found in the samples included in Cluster 2. (The fact that sample 7 is included in this second cluster probably reflects its anomalous nature (see discussion above) and dissimilarity with the "natural" samples upstream from Madrid (Cluster 1), rather than an

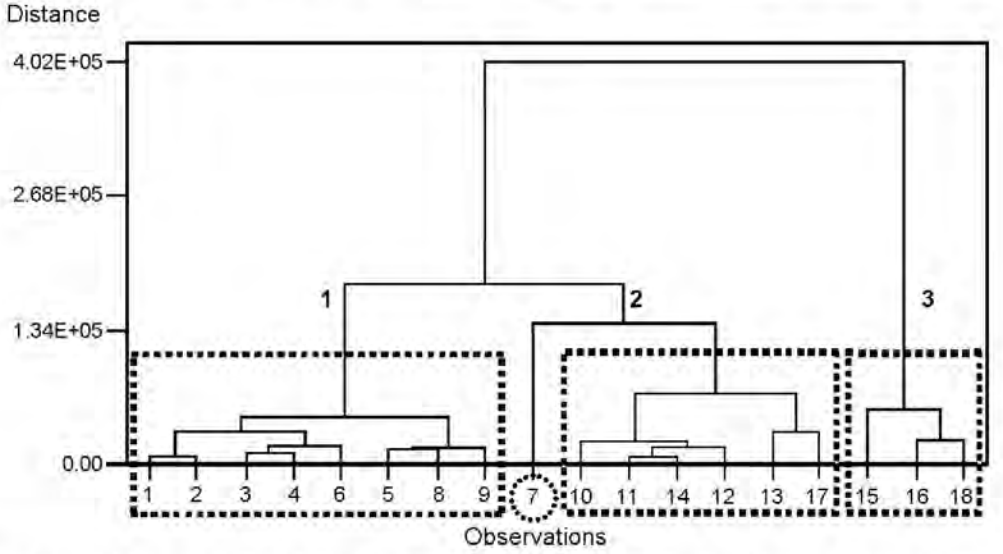

Fig. 2. Cluster analysis of the results (μg g^{-1}) of the "total" digestion (HNO_3, $HClO_4$, HF). (Distance measure: Manhattan; linkage method: Ward). Rectangles mark the three clusters considered in the analysis (Cluster 1: Samples taken upstream from Madrid; Cluster 2: Samples taken inside or downstream of Madrid, with [Ca]<32000 μg g^{-1}; Cluster 3: Samples taken inside or downstream of Madrid, with [Ca]>70000 μg g^{-1}).

Table 5
Centroids (arithmetic mean, in μg g^{-1}) of three clusters resulting from a K-means cluster analysis excluding Ca

Element	Centroids			
	Cluster 1–"natural" Samples 1–9 (except S7)	Cluster 2 Sample 7	Cluster 3–"urban" Samples 10–18	Enrichment Factor (%) Cluster 3/ Cluster 1
Ag	1.5	2	6.6	452
Al	86525	61900	66577	77
As	17	57	24	143
Ba	360	29	284	79
Be	6.4	6	4.7	73
Ce	154	136	129	84
Co	5.1	9	6.4	126
Cr	27	33	48	175
Cu	27	144	101	367
Fe	22137	90800	25956	117
Hg	0.164	0.076	0.805	490
K	26562	21100	27967	105
La	76	66	70	92
Mg	5262	7000	8989	171
Mn	489	1276	386	79
Na	16062	11700	12844	80
Ni	14	33	22	160
P	833	1297	1233	148
Pb	75	207	146	195
Ti	2412	2200	2867	119
V	28	29	34	119
Y	31	26	25	81
Zn	87	182	294	336

intrinsic proximity to the geochemical nature of the "urban" samples in Cluster 2). If the influence of Ca content is removed by excluding this variable from a K-means Cluster analysis in three groups, all samples collected within Madrid's area of influence (samples 10–18) are reunited in one single, "urban" group (Cluster 3), all samples taken upstream of Madrid, and thus unaffected by significant urban discharges, remain grouped in the "natural" Cluster 1, and pyrite-rich sample 7 forms a group—Cluster 2—of its own (Table 5). The dissimilar nature of the sediments in the "urban" and "natural" reaches is manifested in the widely different average concentrations of anthropogenic elements for both groups (enrichment factors in "urban" relative to "natural": Ag, 450%; Cr, 175%; Cu, 365%; Pb, 195%; and Zn, 340%). In contrast, most major elements (Fe, K, Na, Ti) and essentially geogenic trace elements (Ce, La, Y) show fairly uniform concentrations in both clusters, or slightly higher in the "natural" group.

As opposed to the classification derived from the Cluster Analysis, which is based on the varying degree of urban influence on the sediments, the concentration of Al, Ca and Mg are directly related to the lithology along each section of the Manzanares basin. In the northern, upper part of its basin the river runs through a granitic mountainous area until it meets the alluvial materials (gravel, sand and silt) to the north of Madrid and south of the mountain range. The silicate nature of these geologic formations is reflected in high Al and relatively low (when compared to the carbonate materials found further south) Ca and Mg concentrations in the sediments (86500, 6150, and 5260 μg g^{-1}, respectively). As the river exits the culverted reach within the boundaries of Madrid, it flows through a landscape of limestone and gypsum-rich marl. Consequently, the sediments to the south–east of the city present higher Ca and Mg contents (38500 and 9000 μg g^{-1}, respectively) and lower levels of Al (66500 μg g^{-1}).

These influences, anthropogenic (or "urban") and geogenic (or "natural") are underscored by the results of a Factor Analysis for the "total" digest, shown in Table 6. Four factors explain most of the variability (82%) of the data. The first factor seems to reflect the "urban" contribution to the elemental composition of the sediment. It comprises the variables Ag, Cr, Cu, Pb

Table 6
Factor Analysis of the results (μg g^{-1}) of the "total" digestion (HNO_3, $HClO_4$, HF) for 16 variables (factor loadings <0.3 have been omitted for clarity)

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Cr	0.938				0.882
Cu	0.924				0.959
Ag	0.913				0.949
Pb	0.891				0.870
Zn	0.886	0.400			0.945
Mg	0.740	0.551			0.855
Ca		0.855			0.827
Na		−0.821			0.849
Al	−0.439	−0.690			0.755
K		0.337			0.171
Mn			0.952		0.957
Fe			0.914		0.898
As	0.308		0.704		0.632
La				0.995	0.999
Ce				0.972	0.992
Y		−0.564		0.660	0.794
% variance	32.5	18.4	16.4	16.1	83.3

Extraction Method: Maximum Likelihood; Rotation: Varimax.

and Zn that exhibit low concentrations before Madrid and much higher ones within and after the city. Enrichment in this same suite of elements has been used in earlier studies to measure the degree of urban disturbance of a soil (De Miguel et al., 1998). The same conclusion seems to apply to river sediments (Birch et al., 2001; Ridgway et al., 2003), a fact that appears to confirm the hypothesis that the elemental combination Ag–Cr–Cu–Pb–Zn is a characteristic marker of the particulate matter generated in and circulating between the different geochemical spheres in urban environments (De Miguel et al., 1999).

The second factor positively groups Ca and Mg, on the one hand, and negatively Al and Na. This factor reveals the nature (carbonate vs. silicate) of the geological material that gives rise to the river sediments. As would be expected, the lowest scores for this factor correspond to samples collected in the granite, sand and silt areas in the north, and they increase towards the south–east where the river flows through carbonate materials. The third factor (Fe–Mn–As) seems to be a manifestation of the process of trace element adsorption by Fe and Mn hydrous oxides. If this assumption were correct, then As would be preferentially retained in the sediment bound to the oxy-hydroxide fraction and would show a higher affinity for this fraction than the other trace elements considered. However, this factor disappears from the results when sample 7 (pyrite-rich core) is excluded from the analysis. The high correlation between As and Fe–Mn that gives rise to the third factor seems to be a statistical artifact related to the anomalous nature of sample 7 and not to a real, underlying phenomenon. Lastly, the fourth factor appears to represent a natural matrix of the sediment that remains fairly constant throughout the whole length of the river, unaffected by changes in lithology or in intensity of urban discharges, and characterised by La, Ce and Y.

The "weak" digestion protocol is assumed to dissolve the fraction of trace elements bound to the carbonate matrix of the sediments, as well as that associated with soluble minerals and exchange sites on clay surfaces (Tessier et al., 1979). The percentage of the "total" metal content extracted in the "weak" digest depends strongly on the proportion of calcite in the sediment and, for the same amount of calcite, varies greatly for the different metals analysed. The influence of the amount of calcium carbonate in the sample on the fraction of metal recovered is particularly significant for Zn (and, to a lesser extent, Cu). In the samples collected from the northern reach of the river, where calcite is essentially absent from the sediment, the amount of Zn extracted does not exceed 10% of the "total" (15% for Cu)—except in sample 5, where it reaches 19%. However, in the final section of the Manzanares, where carbonates are most abundant, recoveries reach 75% for Zn and 54% for Cu.

These results seem to indicate that two different influences on the geochemical constitution of the sediment become superimposed in the samples taken within or downstream of the city. Firstly, these sediments can reach high natural calcite contents (up to 20%), as shown in the results of X-ray diffraction analyses (Table 3). Secondly, they are exposed to effluents from the WWT plants and to uncontrolled discharges of urban runoff. As a result, these sediment samples are enriched in all "urban" elements (i.e. Cr, Cu, Pb and Zn) but particularly in elements like Zn, and to a lesser extent Cu, which have a higher tendency to sorb onto calcite. The interaction of divalent metals with calcite has been extensively investigated (Crockett and Winchester, 1966; Kitano et al., 1976; McBride, 1979, 1980; Franklin and Morse, 1982, 1983; Kornicker et al., 1985; Davis et al., 1987, Zachara et al., 1988; Tesoriero and Pankow, 1996; Parkman et al., 1998). As a result, several mechanisms have been proposed to explain the retention of these elements by calcite surfaces, i.e. adsorption, ion exchange, surface complexation, solid solution precipitation and pure-phase precipitation, depending on factors such as ionic radii and solvation energies of the cations, concentration of metals in solution, recrystallization rates of calcite, etc. In the specific case of Zn, Zachara et al. (1988) concluded that adsorption onto calcite mainly occurs through exchange of Zn^{2+} and $ZnOH^{+}$ with Ca^{2+} in a hydrated layer adsorbed to the calcite surface, and that the surface complex thus formed had a marked covalent character. Thus, the considerable desorption of Zn from the carbonate surface at moderately low pH values observed in our work is attributed by Zachara et al. (1988) to the reversibility of the sorption process in the presence of Ca^{2+} which increases in concentration as the pH of the $CaCO_{3(aq)}$ solution is lowered. This fact indicates that Zn and Cu are the two elements more susceptible to be remobilised from the sediment

and incorporated into the aqueous phase, and that this process is most likely to occur precisely where the highest concentrations of both elements are found, in the southern stretch of the river after it crosses Madrid.

4. Conclusions

The River Manzanares, which in years of low precipitation can carry up to 60% of urban water, constitutes an interesting example of an urban river with a strong anthropic control on its geochemical and hydrodynamic behaviour. Trace element concentrations in the sediments of the Manzanares show local lithological influences superimposed on urban inputs, in the form of treated urban wastewater and uncontrolled discharges of street runoff. The geochemical signature of each of these influences can be determined by means of a K-means Cluster Analysis of the samples and a Factor Analysis of "total" (i.e. HNO_3+$HClO_4$+HF extraction) elemental concentrations in the sediment. The "urban" component of the trace element load is characterised by the Ag–Cr–Cu–Pb–Zn association, individual elements of which show enrichment factors between 200% and 450% after the river enters the city of Madrid. This finding is consistent with earlier studies which suggested that this same suite of elements characterises particulate matter of urban origin and serves as a fingerprint of urban disturbance in soils.

On the other hand, the "natural" component appears to be separated into two factors. Ce, La and Y show fairly constant concentrations all along the river and seem to reveal a "natural" background which is not greatly affected by changes in lithology. These changes, however, are clearly reflected in the concentration of Ca and Mg, on one side, and Al and Na, on the other, which vary strongly as the mineral matrix of the sediment changes from carbonate to silicate.

Although the "total" concentration of trace elements in the sediments of the Manzanares are similar to those found in other urban rivers, toxicological threshold levels for most of these elements are exceeded after the river crosses Madrid, a fact that raises concerns about latent adverse effects on aquatic ecosystems housed in the sediments of this stretch of the river.

The potential mobility and bioavailability of trace elements in the sediments of the Manzanares were evaluated through an NaOHAc+HOAc extraction. The highest extraction rates corresponded to Zn and, to a lesser extent, Cu. Both divalent cations show a high affinity for carbonate materials in the sediment and are easily displaced from the solid matrix and transferred to the aqueous phase. Since the concentration of Ca and Mg carbonate greatly increases in the sediment after the river crosses Madrid where it receives an important input of Cu and Zn, the highest potential for remobilisation and negative environmental impact is expected precisely along this stretch of the river, south of Madrid.

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